Anodized alumina films pigmented with Ni, Cu, and Ni+Cu studied by soft x-ray absorption spectroscopy

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We recorded Cu 2p absorption spectra of pigmented Cu samples at room temperature, 200 ˚C and 500 C°. The measurements at Cu and Ni L_2 and L_3 edges were made at the beam line 7.0.1. X-ray absorption spectra were recorded using x-ray fluorescence-yield-detection mode (FY). The spectra were normalized to a reference signal from a clean gold mesh to correct the intensity fluctuations in the photon beam.

A pure Cu spectra was included as reference as well. Fig.1 exhibits the differences related to different configurations of Cu in 2p XAS spectra of samples prepared at different temperatures. The differences are observed between the spectra of room temperature and at higher temperature due to different oxidation states. The XAS spectrum of Cu at room temperature resembles the spectra of monovalent Cu_2O (1,2). Monovalent Cu has the main peak at around 933.3 eV. It seems that the ground state has in general, predominantly $3d^{10}$ with a little $3d^9 4s$ character. Excitations are possible to reach the empty Cu band with a mixed s,d character and the empty ligand band.

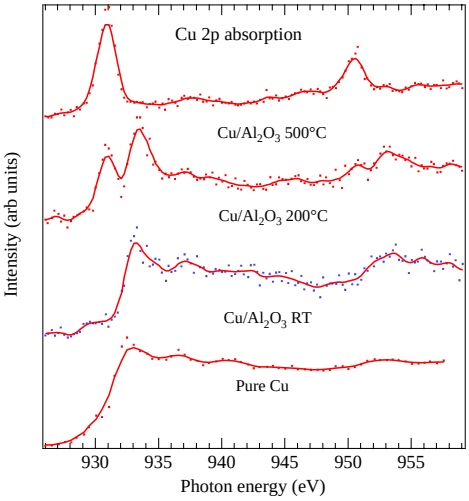

Fig.1 2p absorption of Cu pigmented Al_2O_3 annealed at different temperatures.

The samples annealed at 500 °C behaves like divalent Cu (Cu^{2+}) in CuO. The L_3 edge of divalent Cu has a strong peak at about 931.3 eV. The origin of this feature is understood now (3,4): a Cu 2p electron is excited from the 2p level to the empty 3d bands, but the effect of Coulomb interaction between the strongly localized 2p hole and the rather small Cu 3d orbital is to localize the extra 3d electrons. Similar peaks are expected whenever a core electron is excited to into a narrow (d) band and have been found in many transition metal compounds (3). The spectra of monovelant Cu at room temperature do not show such peak because the d shell is essentially filled.

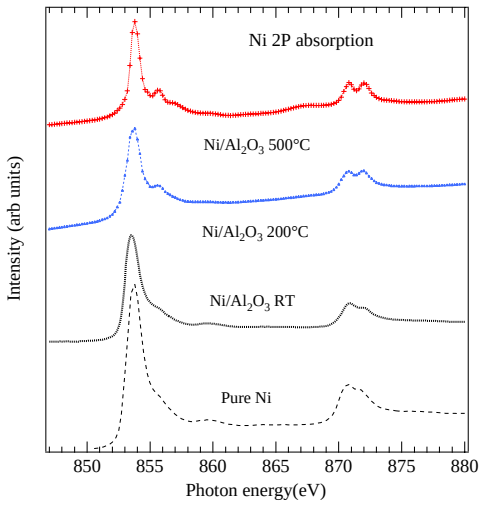

Fig.2 Ni 2p absorption of Ni-pigmented Al_2O_3 anealed at different temperatures.

Looking at 200 °C (which is a temperature between room temperature

and 500 °C), it was observed that it behaves in between monovalent and divalent Cu. In presence of Cu 2p hole the excitation to the empty s,d band give rise to the main peak at 933.4 eV. The smaller peak at around 931.3 eV is most likely due to Cu^{2+} contribution.

Fig.2. shows an x-ray absorption spectrum of Ni $L_{2,3}$ region of pigmented Ni. These samples have been annealed to 200 °C and 500 °C. The same trend is observed in Ni pigmented samples as was observed in Cu, the difference in oxidation states, from room temperature to 500 °C. The main peaks at 853.6 and 870.0 eV on the photon energy scale are due to the excitation to the $2p^5_{3/2}3d^{10}$ (L_3) and $2p^5_{1/2}3d^{10}$ (L_2) core excited states, respectively. In the $2p_{3/2}$ there is a first sharp peak at 853.6 eV and an about 2 eV higher absorption energy structure which is strongly enhanced by annealing. At $2p_{3/2}$ edge there are two features and the one at higher absorption energy is enhanced at the higher temperatures. The spectrum of Ni at room temperature looks like pure Ni as given in reference (5). The spectrum of Ni at 200 °C is similar to NiO as reported by others (6). Spectra at 500 °C is similar to Ni^{2+}.

Fig.3 shows XAS spectra of Ni+Cu pigmented samples. We did not see any Ni signal but the strong contribution of Cu showing the same trends for different temperatures as discussed above. We know from the deposition process that Ni was there. Very little Ni signal shows up at 500 °C in Ni XAS spectra (not show). We think that there might be some diffusion processes at this temperature which is the reason we can see some Ni coming up otherwise it may be so deep down that cannot be seen through. X-ray emission for Ni+Cu pigmented samples have also been tried because with x-ray emission one can see deeper down but still it was not possible to see any Ni even with this technique. So it was concluded that Ni might have been suppressed during the process of deposition.

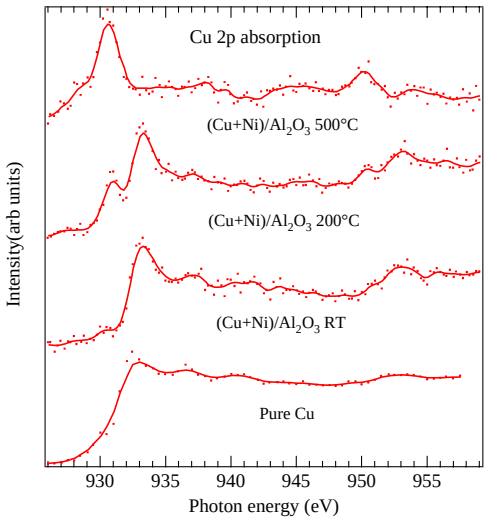

Fig.3 2p absorption of Cu+Ni pigmented Al_2O_3 showing strong contribution of Cu.

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